A Tough Pearl to Crack

Artificial Ceramic Mimics Mechanical Properties of Mother of Pearl

In a collaboration between the MSD research groups of Tony Tomsia and Robert Ritchie, the structure of mother of pearl has been mimicked to create what may well be the toughest ceramic ever produced. The new material combines a ceramic phase and a polymer or metal phase to create a hybrid which is 300 times tougher than its constituent components.

The quest for more energy-efficient technologies necessitates the development of lightweight, high-performance structural materials with exceptional strength (resistance to deformation) and toughness (resistance to fracture). Unfortunately, these two properties tend to be mutually exclusive, and attaining optimal mechanical performance is invariably a compromise between the two. On the other hand, Nature has the ability to combine brittle minerals and organic molecules into hybrid composites with exceptional fracture resistance and structural capabilities. For example, mother of pearl, or nacre, the inner lining of the shells of abalone and certain other mollusks, is renowned not only for its iridescent beauty but also for its exceptional toughness. It combines 95% aragonite, a hard but brittle calcium carbonate mineral, and 5% soft organic molecules producing a material some 3,000 times (in energy terms) more resistant to fracture than aragonite. No human-synthesized composite outperforms its constituent materials by such a wide margin. It is, however, not easy to replicate nacre's remarkable properties; its strength lies in its structural architecture that varies over lengths of scale ranging from nanometers to micrometers. To date, human engineering has not been able to replicate these multiple length scales and the resulting performance in a single material.

Two years ago, Tomsia and Eduardo Saiz developed a method to produce complex structural architectures through a processing technique that involves the freezing of seawater (MSD Highlight 06-09). When seawater freezes, ice crystals form a scaffolding of thin layers of pure water ice interspersed with impurities such as the salt and microorganisms, which are expelled from the freezing water and entrapped in the space between the ice layers. To adapt this natural process for materials synthesis, ceramic particles are suspended in water. Upon freezing, they are, as expected, expelled from the growing ice crystals and accumulate in the spaces between them. When the ice is sublimated, a porous ceramic remains. Then, the pores can be filled with other materials to form composites.

In this study, a further refinement of the process, a suspension of alumina in water was frozen on a "cold finger," which promotes the formation of lamellar ice. After the ice was removed, a porous ceramic formed with oriented thin alumina plates. The spaces between the plates were filled with a well-known polymer, PMMA which acts as an internal lubricant. When a load is applied to this material, the hard alumina layers slide (by a small amount), thus dissipating strain energy and increasing toughness. To further increase strength, a nacre-like "brick-and-mortar" structure with very high alumina content was developed. This was done by collapsing the scaffolds in a direction perpendicular to the layers and then sintering the resulting alumina "bricks" to promote brick densification and the formation of ceramic bridges between individual bricks. The end result is a bulk hybrid ceramic-based material whose high specific strength and toughness, ~200 MPa and ~30 $MPa{\cdot}m^{1/2}$, are comparable to those of aluminum alloys. What is unique about this composite is that only the hard ceramic carries the load and provides for strength. The polymer "lubricant" dissipates high stresses and is the origin of the exceptional toughness.

The unique hierarchical design of these materials is amenable to many structural systems. To achieve higher temperature structural materials, the researchers are currently replacing the polymer "lubricant' phase with a high melting point metal; by controlling its interaction with the ceramic, they hope to improve strength as well as the toughness at elevated temperatures.

A. P. Tomsia (510) 486-4918; E. Saiz, (510) 486-6202; R. O. Ritchie (510) 486-5798, Materials Sciences Division (510 486-4755), Berkeley Lab.

E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, "Tough, Bio-Inspired Hybrid Materials," Science **322** 1519 (2008).

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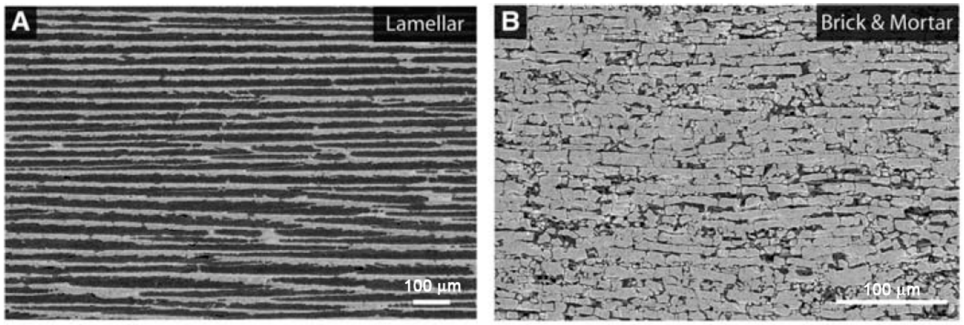
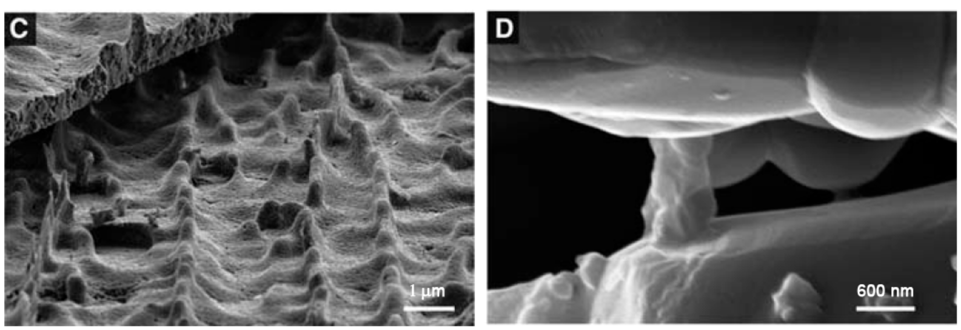
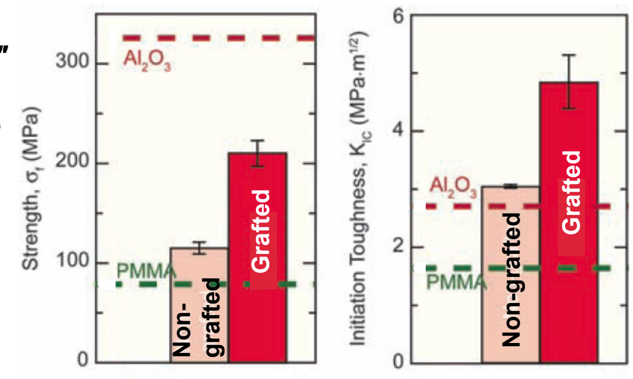


***Structure of ice-templated materials**. Initial directional freeze-casting produces a lamellar composite of alumina (Al_2O_3, light phase) and a polymer PMMA. A nacre-like "brick and mortar" architecture (above, right) is prepared through the pressing of the lamellar materials and subsequent sintering; the ceramic content is increased up to 80 vol. %, increasing strength.*

***Structure is controlled on the sub-micron scale** to increase toughness. Adding sucrose to the freeze-casting slurry allows the microroughness of the alumina to be adjusted. In the sintering step sub-micron bridges are formed (below, right) which limit sliding of the "bricks" under load.*



***"Molecular grafting"** promotes chemical bonding between the alumina and PMMA, increasing both strength and toughness of the composite. The toughness (right) is greater than that of either of the individual components.*



***Detailed fracture measurements** show that the "bricks and mortar" alumina/PMMA hybrid displays increased toughness as cracks propagate (below, left). The highest values, 30 MPa $m^{1/2}$ are 300 times that (in energy terms) of alumina and are far in excess of that predicted from a "rule of mixtures" (below right).*